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<b>(51) International Patent Classification <sup>5</sup> :</b> <b>H01M 4/48, 10/36</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/08612</b> <b>(43) International Publication Date:</b> 29 April 1993 (29.04.93)
<b>(21) International Application Number:</b> PCT/GB92/01787 <b>(22) International Filing Date:</b> 29 September 1992 (29.09.92)  <b>(30) Priority data:</b> 9121912.1 16 October 1991 (16.10.91) GB  <b>(71) Applicant (for all designated States except US):</b> UNITED KINGDOM ATOMIC ENERGY AUTHORITY [GB/GB]; Harwell Laboratory, Oxfordshire OX11 0RA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> NEAT, Robin, John [GB/GB]; 37 Lodge Close, Old Marston, Oxford OX3 0QP, Oxfordshire (GB). MACKLIN, William, James [GB/GB]; 33 Thackley End, 119 Banbury Road, Oxfordshire, Oxford OX2 6LB (GB).		<b>(74) Agent:</b> MANSFIELD, Peter, Turquand; United Kingdom Atomic Energy Authority, Patents Branch, Bldg 329, Harwell Laboratory, Oxfordshire OX11 0RA (GB).  <b>(81) Designated States:</b> AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TITANIUM DIOXIDE-BASED MATERIAL  <b>(57) Abstract</b>  Electrochemical insertion of lithium into titanium dioxide initially in its rutile form, the insertion being performed at an elevated temperature (for example 120 °C), produces a material $\text{Li}_x\text{TiO}_2$ with x between 0.5 and 1.0. This material is suitable as an active cathode material in a secondary cell as it can be repeatedly recycled. The material has a crystal structure, different from that of the initial rutile titania, which is believed to be hexagonal.		

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Titanium Dioxide-Based Material

This invention relates to a material based on titanium dioxide, a method of making the material, and to use of  
5 this material in an electrochemical cell.

Titanium dioxide occurs in two forms: anatase and rutile. It has hitherto been found that lithium can be inserted into these two forms to very different extents.  
10 The chemical lithiation of anatase titania with n-butyl lithium results in a maximum stoichiometry of  $\text{Li}_{0.7}\text{TiO}_2$  (see M.S. Whittingham et al., J. Electrochem. Soc., 124, 1388 (1977)), whereas it has been reported that only small amounts of lithium, no more than 2 atomic percent,  
15 can be chemically inserted into the rutile form (see D.W. Murphy et al., Solid State Ionics, 9 & 10, 413 (1983)). The lithiated anatase material  $\text{Li}_x\text{TiO}_2$  has been cycled in an electrochemical cell over the range of x from 0.15 to 0.45 using a lithium perchlorate/propylene carbonate  
20 electrolyte, with an average cell voltage of about 1.7 V (see F. Bonino et al., J. Power Sources, 6, 261 (1981)), whereas rutile titania in such a cell was found to have poor capacity and to have a significantly lower discharge voltage.

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According to the present invention there is provided a material of stoichiometric formula  $\text{Li}_x\text{TiO}_2$ , where x is between 0.5 and 1.0, made by electrochemical insertion at an elevated temperature of lithium into titanium dioxide in  
30 its rutile form. The material is believed to be of hexagonal form.

In a second aspect, the invention provides a method of making a material of stoichiometric formula  $\text{Li}_x\text{TiO}_2$ ,  
35 where x is between 0.5 and 1.0, the method comprising the successive steps of:

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- (i) assembling an electrochemical cell having an anode comprising lithium as active material; a non-aqueous lithium ion conducting electrolyte; and a cathode containing titanium dioxide in its rutile form as active cathode material; and
- (ii) discharging the cell at an elevated temperature such that the cathode material is transformed into material of formula  $\text{Li}_x\text{TiO}_2$ .

10

Preferably the elevated temperature is above  $100^\circ\text{C}$ , for example between  $100^\circ$  and  $150^\circ\text{C}$ , most preferably about  $120^\circ\text{C}$ . Preferably the electrolyte comprises a complex of poly(ethylene oxide) and a lithium salt such as  $\text{LiCF}_3\text{SO}_3$  or  $\text{LiClO}_4$ , this providing a solid-state electrolyte.

15

In a third aspect, the invention provides a rechargeable electrochemical cell comprising an anode comprising lithium as active anode material, a non-aqueous lithium ion conducting electrolyte, and a cathode containing as the active material a material of stoichiometric formula  $\text{Li}_x\text{TiO}_2$ , where  $x$  lies between 0.5 and 1.0, formed by electrochemical insertion of lithium ions into titanium dioxide in its rutile form.

25

It will be appreciated that this cell can be made by the previously defined method of making the  $\text{Li}_x\text{TiO}_2$  material, the material being formed in situ.

30

The invention will now be further described with reference to the accompanying drawings, in which:

35

Figure 1 shows discharge graphs for electrochemical cells incorporating anatase titanium dioxide;

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- Figure 2 shows discharge graphs for electrochemical cells incorporating rutile titanium dioxide;
- 5 Figure 3 shows graphically the variation in capacity with discharge cycle for the cells of Figure 1 and of Figure 2; and
- 10 Figures 4a to d show graphically X-ray diffraction patterns at successive stages during the first discharge of a cell incorporating rutile titanium dioxide.

Experiments have been carried out using the two

15 different forms of titanium dioxide, anatase and rutile. Composite cathodes containing titanium dioxide sample, ketjen carbon black, poly(ethylene oxide)(PEO) (MW 4000000) and  $\text{LiClO}_4$  were prepared by doctor blade casting from the appropriate solvent slurry onto a nickel current collector.

20 The resulting cathodes had the composition 45 vol.% titanium dioxide, 5 vol.% carbon and 50 vol.% PEO- $\text{LiClO}_4$  ( $[\text{EO units}]/[\text{Li}] = 12$ ) with a capacity of about 1 mA h  $\text{cm}^{-2}$  based on a value of 335 mA h  $\text{g}^{-1}$ , (corresponding to the insertion of one lithium into

25  $\text{TiO}_2$ ). Sheets of the electrolyte PEO- $\text{LiClO}_4$  ( $[\text{EO units}]/[\text{Li}] = 12$ ) were cast from acetonitrile solution onto silicone release paper. Solid state cells containing a lithium foil anode with an active area of 40  $\text{cm}^2$  were constructed in a dry room ( $T = 20^\circ\text{C}$ , dewpoint temperature

30  $-30^\circ\text{C}$ ) and assembled using a combination of heat and pressure, each cell consisting of a nickel foil current collector, a composite cathode layer about 36 microns thick, a polymer electrolyte layer about 85 microns thick, and a lithium foil 100 microns thick. The cells were

35 packaged and placed in an oven at  $120^\circ\text{C}$  for testing.

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Measurements of a.c. impedance of the two types of cell after 2 hours in the oven indicated that those incorporating rutile had an overall impedance several times larger than that of the anatase cells. This is consistent with the lower electronic conductivity of the rutile material. The open-circuit voltages for both anatase and rutile cells were in the region 2.4 - 2.6 V.

The cells were then discharged, and cycled using a computer-controlled charge/discharge apparatus in a constant current mode between preset voltage limits, all at a constant temperature of 120°C. Initial cell cycling was carried out between the voltage limits 3.0 V and 1.2 V at the C/8 rate (i.e. at such a rate as to discharge it completely after 8 hours if it were 100% efficient).

Referring to Figure 1 there are shown graphically the 1st, 2nd, 10th and 20th discharge curves for the anatase cells. The primary discharge of anatase results in two distinct plateaux. The first at 1.78 V continues up to the composition  $\text{Li}_{0.6}\text{TiO}_2$ ; the final composition is  $\text{Li}_{1.0}\text{TiO}_2$ , corresponding to a theoretical energy density of about 565 W h  $\text{kg}^{-1}$ . The shape of the second discharge curve resembles that of the first, albeit at a lower capacity, implying that the anatase structure is retained following the initial insertion of lithium ions. This has been confirmed by X-ray diffraction where the pattern obtained from an anatase cathode taken from a cell discharged to a depth  $\text{Li}_{0.7}\text{TiO}_2$  is essentially the same as that obtained from an uncycled cathode. The cause of the poor capacity retention in the anatase material that occurs during cycling has not been established.

Referring now to Figure 2 there are shown graphically the 1st, 2nd, 10th and 20th discharge curves for the rutile cells. The initial discharge has a short step at about

- 5 -

1.75 V that can be attributed to a small quantity of anatase impurity in the rutile sample, with the majority of the discharge capacity (about 90%) occurring between 1.50 and 1.40 V. Complete discharge to a 1.2 V cutoff gives a final composition  $\text{Li}_{1.0}\text{TiO}_2$  corresponding to a theoretical energy density of about  $500 \text{ W h kg}^{-1}$ . (The insertion of one lithium per titanium into  $\text{TiO}_2$  rutile in this lithium polymer electrolyte cell is in complete contrast to the very low levels of lithium successfully incorporated into rutile titanium dioxide at ambient temperature). The second discharge shows a cell voltage that decreases continuously with capacity to a value approximately half that obtained in the initial discharge (i.e. cycling of  $\text{Li}_x\text{TiO}_2$  where x varies between 0.5 and 1.0). The average cell voltage of 1.73 V corresponds to a theoretical energy density of about  $290 \text{ W h kg}^{-1}$ . The subsequent discharge curves are all very similar both in terms of shape and capacity.

Referring now to Figure 3, the variation in the capacity of the two types of cell with cycle number is shown graphically for the first thirty cycles. It is apparent that the lithiated rutile material has excellent reversibility. Indeed the rutile cells have been found to suffer very little decrease in capacity after as many as 250 cycles, even at a C or C/2 discharge rate.

Referring now to Figure 4, X-ray diffraction patterns have been obtained for composite cathodes removed from cells made with rutile titanium dioxide discharged to different depths. These patterns were obtained with a diffractometer employing copper K-alpha radiation and incorporating pulse height discrimination and a curved graphite secondary monochromator, data collection and processing over the range for  $2\theta$  from 10 to 70 degrees being computer controlled. Figure 4(a) shows the pattern

from undischarged rutile  $\text{TiO}_2$ . Figure 4(b) shows the pattern from a composite cathode discharged to the composition  $\text{Li}_{0.25}\text{TiO}_2$ , where the rutile structure is clearly intact. (The peaks appearing at  $2\theta$  values of  $19.0^\circ$  and  $23.5^\circ$  are associated with the crystalline polymer). At 50% depth of discharge, Figure 4 (c), that is at a composition of  $\text{Li}_{0.5}\text{TiO}_2$ , there is a drastic reduction in the intensity of the strongest rutile reflection at  $27.5^\circ$  with the predominant phase being an unidentified lithium titanium oxide characterised by the d-spacings given in Table 1. (The composite nature of the cathode samples limits the quality of the X-ray diffraction data and so only major reflections are given). At a composition  $\text{Li}_{0.8}\text{TiO}_2$ , Figure 4 (d), the majority phase has a X-ray diffraction pattern similar to that of a hexagonal form of  $\text{LiTiO}_2$  first reported by Hewston and Chamberland (see J.Phys. Chem. Solids, Vol. 48, No. 2, 97 (1987)), while the peaks associated with the unidentified phase seen at composition  $\text{Li}_{0.5}\text{TiO}_2$  have disappeared. The intercalation of lithium into  $\text{TiO}_2$  rutile appears to occur via an intermediate phase of approximate composition  $\text{Li}_{0.5}\text{TiO}_2$  that on further lithiation leads to the formation of a hexagonal form of  $\text{LiTiO}_2$ . Presumably the activation barrier to the formation of the intermediate phase precludes its formation at ambient temperature.

Table 1

30 X-ray Diffraction Data for  $\text{Li}_{0.5}\text{TiO}_2$

	Intensity	Interplanar spacing/nm
	95	.344
35	100	.249
	65	.222
	80	.174



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A significant decrease in cell resistance, from about 5 ohms to about 1 ohm, is observed during the first discharge of the  $\text{TiO}_2$  rutile cells in the region up to a composition about  $\text{Li}_{0.5}\text{TiO}_2$ , while during subsequent cycling the cell resistance is essentially independent of the state of discharge. This is consistent with the initial resistance drop being associated with a structural transformation of the  $\text{TiO}_2$  rutile such as that described above resulting in a material of higher conductivity. A similar decrease in cell resistance is not observed during the first discharge of the anatase  $\text{TiO}_2$  cells.

It is thus apparent that one mole of lithium can be electrochemically intercalated into both anatase and rutile polymorphs of  $\text{TiO}_2$  in a lithium polymer electrolyte cell operating at  $120^\circ\text{C}$ . On cycling the anatase form demonstrates poor capacity retention. During the initial discharge the rutile material undergoes a structural transformation resulting in the formation of a hexagonal form of  $\text{LiTiO}_2$ . This hexagonal  $\text{LiTiO}_2$  prepared in situ from rutile exhibits excellent reversibility over the composition range  $\text{Li}_x\text{TiO}_2$ , where  $x$  is between 0.5 and 1.0, and good rate performance. The average cell voltage is about 1.73 V and corresponds to a theoretical energy density of about  $290 \text{ W h kg}^{-1}$ .

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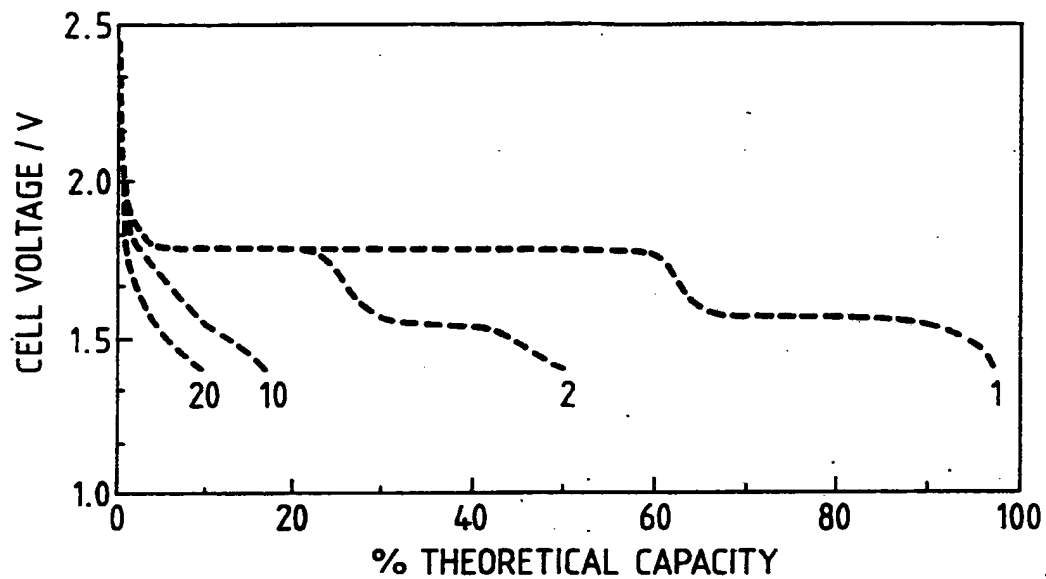
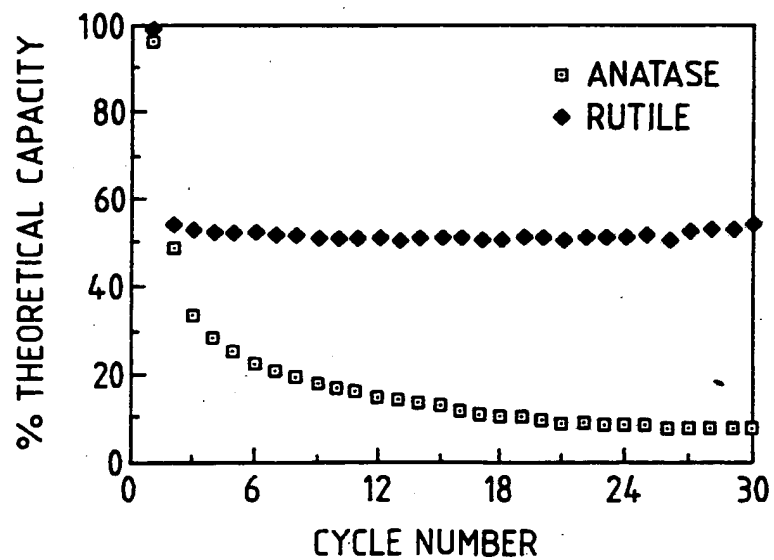
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Claims

1. A material of stoichiometric formula  $\text{Li}_x\text{TiO}_2$ ,  
characterised in that x is between 0.5 and 1.0, and that  
5 the material is made by electrochemical insertion at an  
elevated temperature of lithium into titanium dioxide in  
its rutile form.
2. A material as claimed in Claim 1 wherein the elevated  
10 temperature is between  $100^\circ\text{C}$  and  $150^\circ\text{C}$ .
3. A method of making a material of stoichiometric  
formula  $\text{Li}_x\text{TiO}_2$ , characterised in that x is between 0.5  
and 1.0, and that the method comprises the successive steps  
15 of:
- (i) assembling an electrochemical cell having an anode  
comprising lithium as active material; a non-aqueous  
lithium ion conducting electrolyte; and a cathode  
20 containing titanium dioxide in its rutile form as  
active cathode material; and
- (ii) discharging the cell at an elevated temperature such  
that the cathode material is transformed into material  
25 of formula  $\text{Li}_x\text{TiO}_2$ .
4. A method as claimed in Claim 3 wherein the elevated  
temperature is between  $100^\circ\text{C}$  and  $150^\circ\text{C}$ .
- 30 5. A method as claimed in Claim 4 wherein the elevated  
temperature is about  $120^\circ\text{C}$ .
6. A method as claimed in any one of Claims 3 to 5  
wherein the electrolyte is a solid state electrolyte.

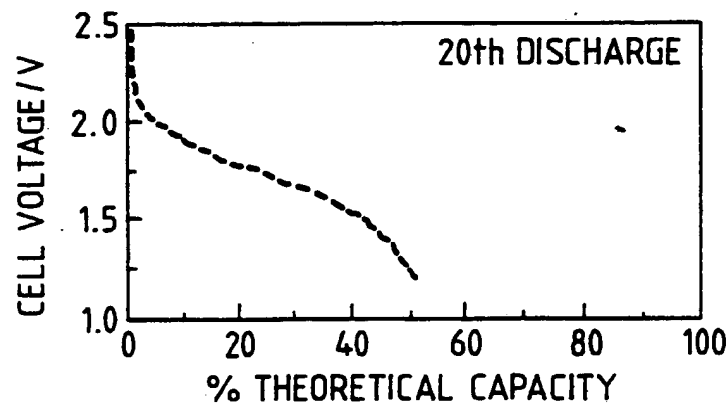
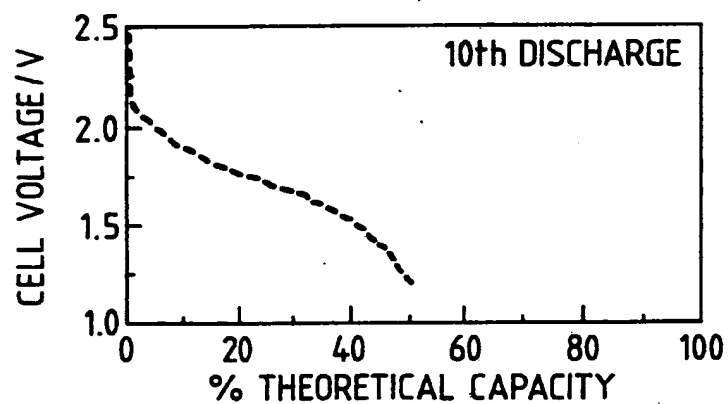
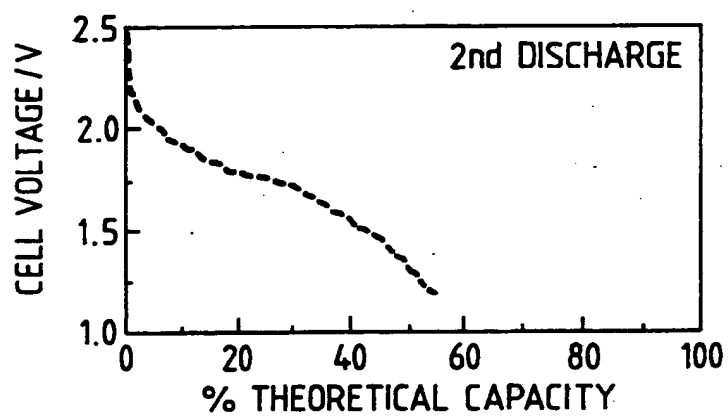
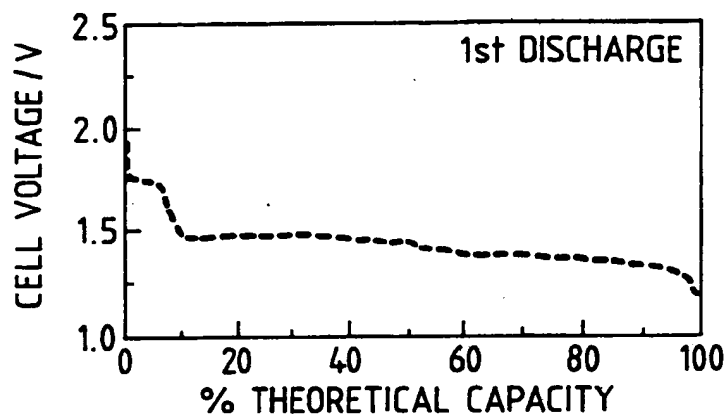
7. A rechargeable electrochemical cell comprising an anode comprising lithium as active anode material, a non-aqueous lithium ion conducting electrolyte, and a cathode containing as the active material a material as claimed in Claim 1 or Claim 2.

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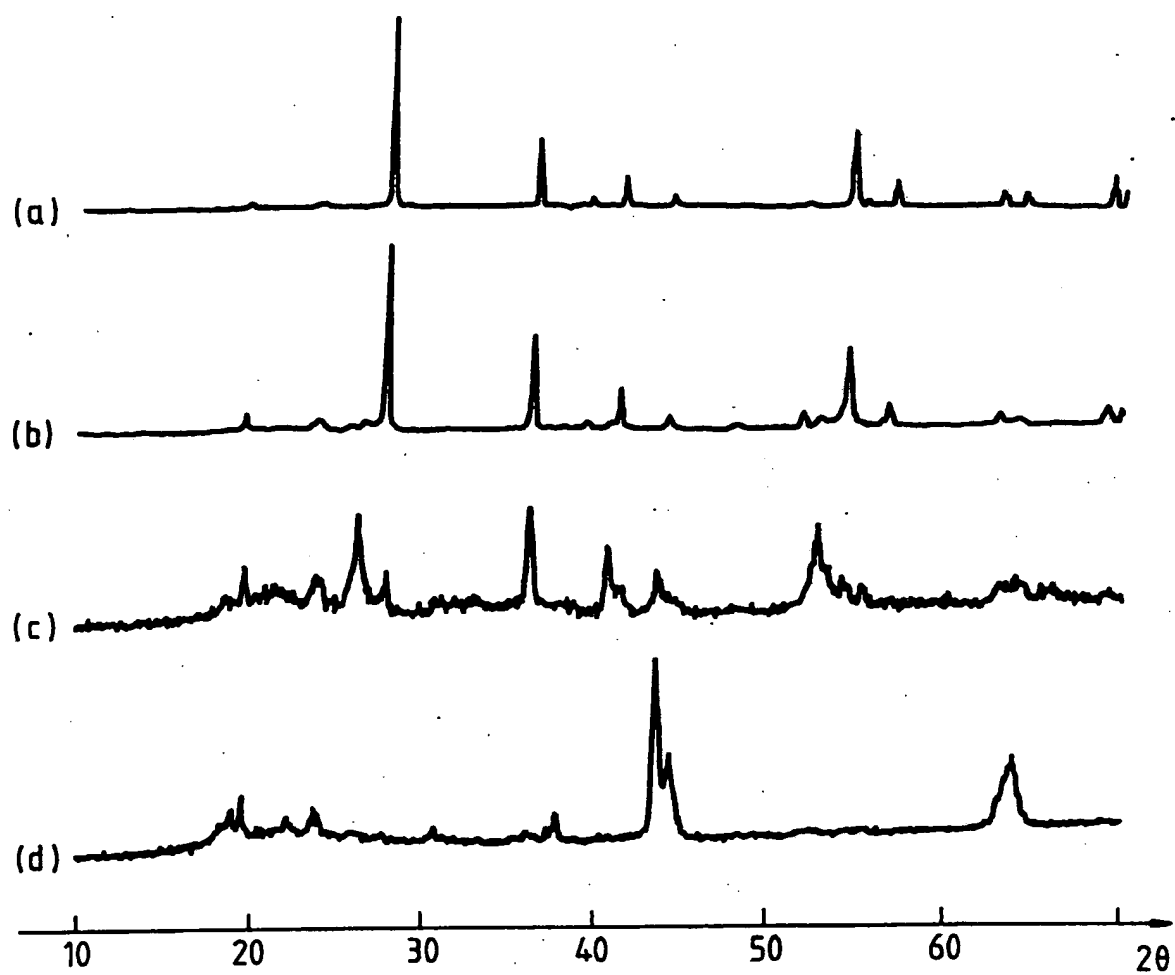
*Fig. 1.**Fig. 3.*

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Fig.2.



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*Fig.4.*

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/01787

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: H 01 M 4/48, 10/36</b>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">IPC5</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">H 01 M</td> </tr> </table> <div style="text-align: center; border: 1px solid black; padding: 2px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	H 01 M								
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IPC5	H 01 M													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 2px;">Category *</th> <th style="width: 60%; padding: 2px;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 30%; padding: 2px;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">JOURNAL OF POWER SOURCES, vol. 20, 1987, K. Kanamura et al: "Diffusion of lithium in the TiO2 cathode of a lithium Battery ", see page 127 - page 134 esp. pages 127, 128</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,3,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">JOURNAL OF POWER SOURCES, vol. 14, 1985, Tsutomu Ohzuku et al: "Electrochemistry of anatase titanium dioxide in lithium nonaqueous cells ", see page 153 - page 166 esp. pages 153, 154</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Patent Abstracts of Japan, Vol 10, No 217, E423, abstract of JP 61- 54165, publ 1986-03-18 (MATSUSHITA ELECTRIC IND CO LTD)</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	JOURNAL OF POWER SOURCES, vol. 20, 1987, K. Kanamura et al: "Diffusion of lithium in the TiO2 cathode of a lithium Battery ", see page 127 - page 134 esp. pages 127, 128	1,3,7	A	JOURNAL OF POWER SOURCES, vol. 14, 1985, Tsutomu Ohzuku et al: "Electrochemistry of anatase titanium dioxide in lithium nonaqueous cells ", see page 153 - page 166 esp. pages 153, 154	1-7	A	Patent Abstracts of Japan, Vol 10, No 217, E423, abstract of JP 61- 54165, publ 1986-03-18 (MATSUSHITA ELECTRIC IND CO LTD)	1-7
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:<sup>10</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search  <b>18th December 1992</b> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report  <b>0 5. 01. 93</b> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">           International Searching Authority    <b>EUROPEAN PATENT OFFICE</b> </td> <td style="border: 1px solid black; padding: 5px;">           Signature of Authorized Officer    <b>Ulla Granlund</b> </td> </tr> </table>			Date of the Actual Completion of the International Search <b>18th December 1992</b>	Date of Mailing of this International Search Report <b>0 5. 01. 93</b>	International Searching Authority  <b>EUROPEAN PATENT OFFICE</b>	Signature of Authorized Officer  <b>Ulla Granlund</b>								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstracts f Japan, Vol 8, No 200, E266, abstract f JP 59- 90360, publ 1984-05-24 (MATSUSHITA DENKI SANGYO K.K.)  —  —————	1-7